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12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The goal of this work is to provide accurate chemical kinetic information on individual reactions for use in Army propellant combustion models. A critical review was prepared, discussing the best data for a number of dark zone species reactions. The effect of the rate coefficients, and their temperature dependence, on the models is described. Experimental and theoretical studies of NH reactions have been made. It is shown that HNO can not be a product of its reactions with CO_2 and H_2O. If it were, nitrate ester combustion would not show dark zones, contrary to the observations. For the NH + H_2 reaction k(833-1432 K) was measured to be $3.5 \times 10^{-11} \exp(-7758 \text{ K}/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

14. SUBJECT TERMS Propellant combustion, models, dark zones, chemical kinetics, temperature dependendence, NH	15. NUMBER OF PAGES 9
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I.   STATEMENT OF THE PROBLEM AND APPROACH

Models of the combustion of nitrate ester and nitramine propellants, especially those for dark zone structures, depend critically on chemical kinetic input data for individual reactions at the temperatures of interest. With the ARO support we have obtained such data for sensitive reactions, in isolation of other reactions, at realistic temperatures for dark zones. One of our HTP (high-temperature photochemistry) reactors, which uniquely allow such studies to be made, was used. Furthermore, an extensive book chapter was prepared.[1] It (i) reviews the current knowledge of the gaseous phase chemistry of propellant combustion, (ii) discusses the rate coefficients and mechanisms of the important individual reactions, and (iii) describes the techniques by which this kinetic input information is obtained for the relevant temperatures.

II.   SUMMARY OF THE MOST IMPORTANT RESULTS

A.   Influence of chemical kinetics on propellant combustion models.

The book chapter[1] extensively discusses the influence of chemical kinetic data on propellant burning models. Included in this are several reactions which, if included with the prior literature rate coefficients, suggested behavior fastly different from what is observed. This is illustrated in Fig. 1 for the CO_2 production from H_2/CO/NO/Ar mixtures at 1000 K. H_2, CO, and NO are all major components of nitrate ester propellant dark zones, DZ. Fig. 1a shows the experimental points obtained by Diau *et al.*[2] for such mixtures at 1000 K. Also shown in the figure is the calculated curve for the CO_2 production using the ARL (Dr. W.R. Anderson) baseline DZ model. Very good agreement is obtained. However, if prior literature data for each of three reactions and,

because of microscopic reversibility, their reverse processes, are included in the models, the results would be at variance with the observations.

Fig. 1b shows the result when the first of these reactions

$$N + CO_2 = NO + CO \tag{1}$$

is added to the baseline mechanism, by using the experimental forward rate coefficients k(T) from Ref. 3 and thermodynamics to compute the rate coefficient of the assumed reverse reaction. The calculated CO_2 production rate now would be two orders of magnitude too fast. If instead

$$NH + H_2O = HNO + H_2 \tag{2}$$

is added, using the forward k(T) of Ref. 4 and the thermochemistry, the predicted rate is about three orders too fast, Fig. 1c. And if the forward k(T) for[4]

$$NH + CO_2 = HNO + CO \tag{3}$$

were similarly added, the rate becomes four orders of magnitude too fast. The result of using these literature values[3,4] in DZ models is that the predicted chemical delay time would be much too short and the DZ length would be reduced such that the DZ would disappear. It therefore appeared that either, **case a,** the reported rate coefficients for reactions (2-4) are too large, or **case b,** the products are not those suggested by these reaction equations. To check these possibilities the chemical kinetic studies summarized in Section II B were performed.

B.   Chemical Kinetic Studies

Both experimental and theoretical investigations have been made. The study of reaction (1) was done under a preceeding ARO grant. No reaction was observable, k_1(285- 1142K) < 5 x 10^{-16} cm^3molecule^{-1}s^{-1},[5] allowing the reaction to be excluded from

the models. The results of the Avramenko study[3] were probably due to the authors'

erroneously attributing the faster N-atom recombination, resulting from the presence of

CO_2 as an inert third-body, to a reaction with this species. As a check on the HTP

method used in our work, another N-atom reaction was studied. For this reaction, $N + O_2$

$= NO + O$, finite reaction rate coefficients were measured. In the lower temperature

range of overlap with earlier works these showed excellent agreement. A subsequent *ab*

initio study of reaction (1) at ARL showed that the barrier in the lowest possible path is

so large that no reaction could have been observed.[6] Thus, reaction (1) is an example of

case a above.

Reactions (2) and (3) have been found in the present work[7] to be examples of **case**

b. In the Rohrig and Wagner study[4] NH was produced in shock waves by HN_3

dissociation. To verify their rate coefficients, we first studied the other reaction reported

in their work

$$NH + H_2 = NH_2 + H \tag{4}$$

In the HTP reactor the NH was produced by the 2-photon 193 nm photolysis of NH_3. We

obtained $k(833\text{-}1432 \text{ K})=3.5 \times 10^{-11}\exp(-7758 \text{ K/T}) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$. This is in such

excellent agreement with their work from 1280 to 1685 K that the results could be

combined to yield $k(833\text{-}1685 \text{ K})=4.4 \times 10^{-11}\exp(-8142 \text{ K/T}) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$. This

made it highly unlikely that there could be a serious error in the k_2 and k_3 measurements

of Ref. 4, thus indicating that the products are probably not $HNO + H_2$ and $HNO + CO$,

respectively. Direct measurements of k_2 and k_3 by the HTP method did not work out as

the photolysis produced O atoms, which react rapidly with the NH. It was therefore

decided to study one of these reactions, i.e. $NH + CO_2$, by *ab initio* means.

Details of the theoretical calculations are also discussed in Ref. 7. The derived potential energy diagram is shown in Fig. 2. The dotted line gives the triplet surface path for the ground state triplet ^{3}NH. Production of HNO + CO by this route involves an energy barrier of 226 kJ mol^{-1}. Alternately, a spin-flip could occur to a singlet surface path. This channel, involving the electronically excited ^{1}NH molecule, is shown by the solid line. This still requires passage over a 126 kJ mol^{-1} barrier to produce HNO + CO. As the measured[4] activation energy is only 60 kJ mol^{-1} it may be concluded that HNO + CO are not the reaction products.

In an attempt to establish what the actual products of the NH+CO$_2$ reaction are, *ab initio* enthalpies for the formation of several adducts were calculated. The most stable of these HONCO is exothermic by only 33 kJ mol^{-1}, which is insufficiently stable to be the final reaction product. It, or another adduct, likely will react further with other species present. Reaction (2) likewise probably involves initial adduct formation. This was not further investigated here. It should be mentioned that H$_3$NO and H$_2$NOH have been suggested[4] as such energetically accessible products of that reaction.

The chemistry problem of the identity of the products of reactions (2) and (3) thus remains. *However, it can be considered as settled that reactions (1-3), with their reverse processes, should not be included in DZ models.*

III.   PUBLICATIONS

A.   In books

W.R. Anderson and A. Fontijn, "Gas-Phase Kinetics for Propellant Combustion Modeling: Requirements and Experiments" in *Overviews of Recent Research on Energetic Materials*, R.W. Shaw, T.B. Brill, and D.L. Thompson, Eds. (World Scientific, London, 2005), pp. 191-239.

B.   In peer–reviewed journals

A. Fontijn, S.M. Shamsuddin, D. Crammond, P. Marshall, W.R. Anderson "Kinetics of the NH Reaction with H_2 and Reassessment of HNO Formation From NH + CO_2, H_2O" *Combustion and Flame* **145**(3)**,** 543-551 (May 2006).

C.   Papers in conference proceedings

A. Fontijn, S.M. Shamsuddin, P. Marshall, and W.R. Anderson "Wide-Temperature Range Kinetics of the NH Reactions with H_2 and CO_2" *2003 Technical Meeting, Eastern States Section, the Combustion Institute*, October 26 – 29, 2003.

IV.   PARTICIPATING SCIENTIFIC PERSONNEL

In addition to the P.I., Dr. Arthur Fontijn, the following people were supported at various times by the grant: Biljana Cosic, who received her Ph.D., William Flaherty, our group technician, Drs. Kevin Cappan and Alexander Ermoline, postdocs, and Duane Crammond, Seth Rios, and Alita Jones, R.P.I. undergraduates.

The following two people contributed in a major way at no cost to the grant:
Dr. William R. Anderson, ARL, whose modeling work suggested the importance of the reactions to be studied, assessed the importance of the results for Army models. I (AF) much appreciate the frequent discussions he and I had throughout the work.
Dr. Paul Marshall, University of North Texas, gave invaluable advice on the theoretical aspects of the work and performed the *ab initio* calculations.

V.   INVENTIONS

None

VI.   BIBLIOGRAPHY

1.   W.R. Anderson and A. Fontijn, "Gas-Phase Kinetics for Propellant and Combustion Modeling: Requirements and Experiments" in *Overviews of Recent Research on Energetic Material*s, R.W. Shaw, T.B. Brill, and D.L. Thompson, Eds. (World Scientific, London, 2005), Chap. 7.

2.   E.W. Diau, M.J. Halbgewachs, A.R. Smith, and M.C. Lin, *Int. J. Chem. Kinet.* **27**, 867 (1995).

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6.   M.R. Manaa and C.F. Chabalowski, *Chem. Phys. Lett.* **300**, 619 (1999).

7.   A. Fontijn, S.M. Shamsuddin, D. Crammond, P. Marshall, and W.R. Anderson, *Combust. Flame* **145**, 543 (2006).
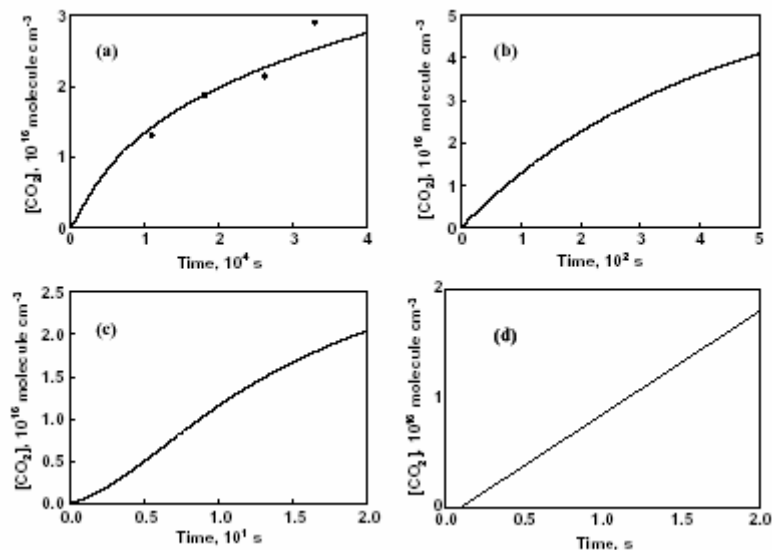
Fig. 1. Comparison of experimental[2] and modeling results[1] for an $H_2/CO/NO/Ar$ mixture at 1000 K. Note the different timescales in (a)-(d).

(a)   Experimental results (points) and modeling result using the baseline mechanism (curve).

(b)   Modeling result when $N + CO_2 = NO + CO$ (1) is added to the baseline mechanism, using the experimental forward k(T) from Ref. 3 and thermodynamics to compute the rate of the assumed reverse reaction.

(c)   Modeling result when $NH + H_2O = HNO + H_2$ (2) is added to the baseline mechanism, using experimental forward k(T) from Ref. 4 and thermodynamics to compute the rate of the assumed reverse reaction.

(d)   Modeling result when $NH + CO_2 = HNO + CO$ (3) is added to the baseline mechanism, using the experimental forward k(T) from Ref. 4 and thermodynamics to compute the rate of the assumed reverse reaction.
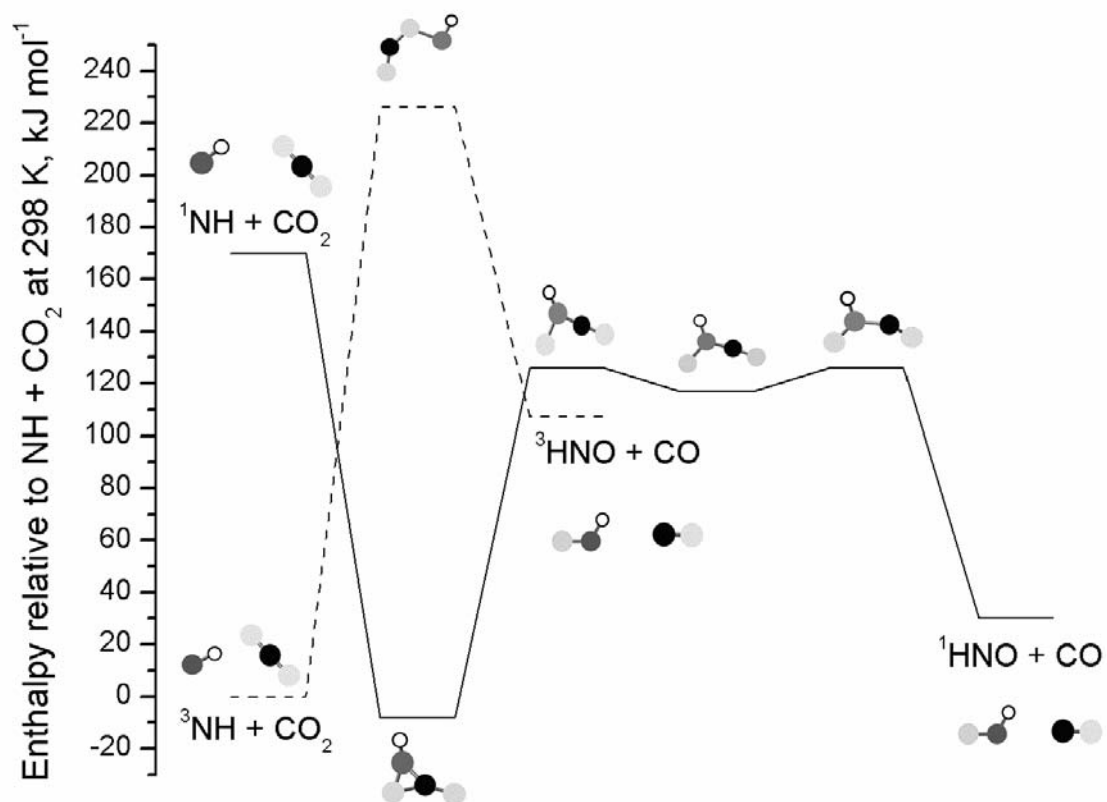
Fig. 2. Potential energy diagram for NH+CO₂ showing paths to HNO+CO. The solid line shows the singlet path, the dashed line the triplet path.